



## DECLARATION

I, Atsuko Ikeda, residing at 26-2-906, Ojima 3-chome, Koto-ku, Tokyo, Japan, do hereby certify that I am conversant with the English and Japanese languages and am a competent translator thereof. I further certify that to the best of my knowledge and belief the attached English translation is a true and correct translation made by me of U.S. Provisional Patent Application No. 60/445,820 filed on February 10, 2003.

I further declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Signed this 29th day of February, 2004

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[NAME OF DOCUMENT]            Specification

[TITLE OF THE INVENTION]

Production Method of Solid Electrolytic Capacitor

[DETAILED DESCRIPTION OF THE INVENTION]

[0001]

[Technical Field to Which the Invention Belongs]

The present invention relates to a solid electrolytic capacitor with low equivalent series resistance (ESR) and high reliability, and a production method of the capacitor.

[0002]

[Background Art]

The capacitor for use in electronic devices such as cellular phone and personal computer is demanded to have a large capacitance with a small size. Among these capacitors, a tantalum solid electrolytic capacitor has a large capacitance for the size and also has good performance and therefore, this capacitor is being preferably used. In order to more increase the capacitance, studies are made on a solid electrolytic capacitor using a dielectric layer mainly comprising niobium oxide having a higher dielectric constant. This niobium-based solid electrolytic capacitor is constituted such that the anode is niobium monoxide, niobium, an alloy mainly comprising niobium, or a mixture of niobium monoxide with niobium or an alloy mainly comprising niobium, the dielectric layer is

a layer formed by electrolytic oxidation of the anode and mainly comprising niobium oxide, and the cathode is a semiconductor. For obtaining good ESR value of the capacitor, it is studied to use a highly electrically conducting organic semiconductor as the semiconductor. However, when a highly electrically conducting organic semiconductor is used for the cathode of a solid electrolytic capacitor and the produced capacitor is packaged on a circuit board or the like, there arises a problem that the leakage current (hereinafter, sometimes simply referred to as "LC") value of the capacitor greatly increases due to heat of soldering at the packaging.

[0003]

[Problems to be Solved by the Invention]

An object of the present invention is to provide a niobium-based solid electrolytic capacitor where when a highly electrically conducting organic semiconductor is used for the cathode of the niobium-based solid electrolytic capacitor and the produced capacitor is packaged on a circuit board or the like, the leakage current value of the capacitor does not greatly increase due to heat of soldering at the packaging, and also provide an electronic circuit and an electronic device each using the capacitor.

[0004]

[Means to Solve the Problems]

As a result of intensive investigations for solving the above-described problem, the present inventors have found that the increase of LC at packaging is ascribable to the thermal instability of the dielectric layer and when an operation of remedying the thermal deterioration of LC is applied two or more times at the formation of the dielectric layer, the problem can be solved. The present invention has been accomplished based on this finding.

That is, the present invention relates to a method for producing a solid electrolytic capacitor, a solid electrolytic capacity obtained by the method, and an electronic circuit and an electronic device each using the solid electrolytic capacitor, which are described below.

[0005]

[1] A method for producing a solid electrolytic capacitor comprising an anode, a dielectric layer and a cathode formed on the dielectric layer, the anode being at least one member selected from niobium monoxide, niobium and an alloy mainly comprising niobium, or a mixture of niobium monoxide with niobium or an alloy mainly comprising niobium, the dielectric layer being a layer formed by the electrolytic oxidation (electrochemical formation) of the anode, and the cathode being an organic semiconductor, the

method comprising sequentially repeating twice or more a step of exposing the dielectric layer to a temperature of 200 to 1,000°C before formation of the cathode and a step of re-electrochemically forming the dielectric layer.

[2] The method for producing a solid electrolytic capacitor as described in [1], wherein the step of exposing the dielectric layer to a temperature of 200 to 1,000°C is performed while supplying water vapor.

[3] The method for producing a solid electrolytic capacitor as described in [1] or [2], wherein the step of exposing the dielectric layer to a temperature of 200 to 1,000°C is performed while supplying oxygen gas of 5% or more.

[4] The method for producing a solid electrolytic capacitor as described in any one of [1] to [3], wherein the leakage current value of the dielectric layer after re-electrochemical formation is 1 nA/CV or less.

[5] A solid electrolytic capacitor produced by the production method described in any one of [1] to [4].

[6] An electronic circuit using the solid electrolytic capacitor described in [5].

[7] An electronic device using the solid electrolytic capacitor described in [5].

[0006] .

[Mode for Carrying Out the Invention]

One embodiment of the method for producing a capacitor of the present invention is described below.

The anode for use in the present invention is principally a sintered body obtained by sintering a powder of niobium monoxide, niobium, an alloy mainly comprising niobium or a mixture of niobium monoxide with niobium or an alloy mainly comprising niobium or by sintering a slurry containing the powder. This powder is produced by a conventionally known method (see, for example, JP-T-2000-600284 (the term "JP-T" as used herein means a "published Japanese translation of a PCT patent application") and Japanese Patent Application Nos. 2001-375128 and 2002-125083).

[0007]

The production method of the sintered body for use in the present invention is not particularly limited, but the sintered body is obtained, for example, by press-molding the powder into a predetermined shape and heating it at 500 to 2,000°C for a few minutes to a few hours under  $10^{-1}$  to  $10^{-5}$  Pa. The specific surface area of the sintered body for use in the present invention is generally from 0.2 to 7 m<sup>2</sup>/g.

[0008]

At the stage of the molded article before sintering or after the molded article is sintered, the sintered body is electrically or mechanically connected with a lead wire formed of a material selected from niobium, partially nitrated niobium, partially oxidized niobium, and tantalum.

The dielectric layer formed on the surface of the sintered body (anode) is a layer mainly comprising niobium oxide. This layer mainly comprises  $\text{Nb}_2\text{O}_5$  and in some cases,  $\text{NbO}_2$  is partially present. The dielectric layer is formed by the electrolytic oxidation (also called "electrochemical formation") of the sintered body (anode). For example, the electrochemical formation is performed by a conventionally known method of dipping the anode in a solution of an acid (e.g., phosphoric acid) or an acid containing a salt and applying a voltage between the anode and a separately prepared metal plate for cathode, such as Ta or platinum.

[0009]

In the present invention, the anode having thereon a dielectric material is exposed to a temperature of 200 to 1,000°C, preferably a temperature of 200 to 500°C where the environment for preventing excessive oxidation of the anode is easily provided, more preferably a temperature of 230 to 500°C where the purpose can be achieved within a relatively short time, the dielectric layer is then re-

electrochemically formed, and these steps of high-temperature treatment and re-electrochemical formation are further repeated once or more, whereby the dielectric layer is stabilized.

[0010]

This exposure to a high temperature is performed for 10 seconds to 100 hours. The exposure to a high temperature may be performed in an atmosphere of air or a gas such as Ar, N and He, and also may be performed under reduced pressure, atmospheric pressure or applied pressure. However, when the high-temperature treatment is performed while supplying water vapor of 0 to 100%, supplying oxygen gas of 5% or more, or supplying water vapor and oxygen gas of 5% or more at the same time, in this order or in the reverse order, the stabilization of the dielectric layer more proceeds and the leakage current (LC) value after packaging of the produced capacitor is more improved.

[0011]

The oxygen gas of 5% or more can be prepared, for example, by a method of diluting oxygen gas with a gas such as Ar, N and He. The water vapor can be supplied, for example, by a method of supplying water vapor generated due to heat from a water reservoir placed in the heat-treatment furnace.

In the above, the maximum temperature at the time of



exposing the anode having thereon a dielectric material to a high-temperature atmosphere is described, but before reaching this temperature, the temperature of the anode having thereon a dielectric material may be gradually elevated from a low temperature to reach the maximum temperature. The method for elevating the temperature may be arbitrarily selected. Incidentally, there arises no problem even when the above-described maximum temperature undergoes fluctuation due to properties of the apparatus, for example, fluctuation of about  $\pm 50^{\circ}\text{C}$ . Also, the temperature may be set to give an artificial thermal fluctuation at the maximum temperature and this basically causes no problem.

[0012]

The re-electrochemical formation may be performed in the same manner as the above-described method for forming the dielectric layer. The LC value after re-electrochemical formation (LC value after final re-electrochemical formation) varies depending on the kind of the sintered body, but based on the CV value (product of electrochemical forming voltage and the volume of the sintered body at that time) of a normal sintered body, the LC value is suitably 1 nA/CV or less, preferably 0.5 nA/CV or less, more preferably 0.3 nA/CV or less. With this LC value, the produced electrolytic capacitor is advantageously more

improved in the initial LC performance. The re-electrochemical formation time is selected so that the above-described LC value can be achieved. The LC value after re-electrochemical formation as used in the present invention is an LC value measured with a voltage of 0.7 times the re-electrochemical forming voltage.

[0013]

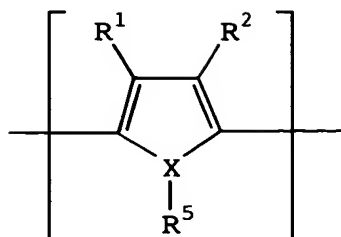
The number of operations of repeating the high-temperature treatment and re-electrochemical formation steps varies depending on the CV value of powder used, the size of anode, the thickness of dielectric layer, or the like and this is determined by previously performing a preliminary experiment.

[0014]

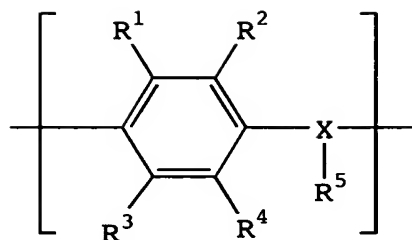
Specific examples of the organic semiconductor used as the cathode in the present invention include an organic semiconductor comprising benzopyrroline tetramer and chloranile, an organic semiconductor mainly comprising tetrathiotetracene, an organic semiconductor mainly comprising tetracyanoquinodimethane, and an organic semiconductor mainly comprising an electrically conducting polymer obtained by doping a dopant to a polymer containing a repeating unit represented by the following formula (1) or (2):

[0015] .

[Chem. 1]



(1)



(2)

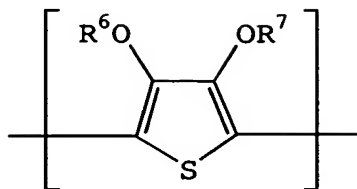
[0016]

wherein R<sup>1</sup> to R<sup>4</sup>, which may be the same or different, each independently represents hydrogen, an alkyl group having from 1 to 6 carbon atoms or an alkoxy group having from 1 to 6 carbon atoms, X represents an oxygen atom, a sulfur atom or a nitrogen atom, R<sup>5</sup> is present only when X is a nitrogen atom, and represents hydrogen or an alkyl group having from 1 to 6 carbon atoms, and each of the pairs R<sup>1</sup> and R<sup>2</sup>, and R<sup>3</sup> and R<sup>4</sup> may combine with each other to form a ring structure.

Preferred examples of the electrically conducting polymer containing a repeating unit represented by formula (1) for use in the present invention include an electrically conducting polymer containing a structure unit represented by the following formula (3) as a repeating unit:

[0017]

[Chem. 2]



(3)

[0018]

wherein R<sup>6</sup> and R<sup>7</sup> each independently represents a hydrogen atom, a linear or branched, saturated or unsaturated alkyl group having from 1 to 6 carbon atoms, or a substituent for forming at least one 5-, 6- or 7-membered saturated hydrocarbon ring structure containing two oxygen elements when the alkyl groups are combined with each other at an arbitrary position, and the ring structure includes a structure having a vinylene bond which may be substituted, and a phenylene structure which may be substituted.

[0019]

The electrically conducting polymer containing such a chemical structure is being electrically charged and a dopant is doped therein. For the dopant, known dopants can be used without limitation.

Examples of the polymer containing a repeating unit represented by formula (1), (2) or (3) include polyaniline, polyoxyphenylene, polyphenylene sulfide, polythiophene,

polyfuran, polypyrrole, polymethylpyrrole, and substitution derivatives and copolymers thereof. Among these, preferred are polypyrrole, polythiophene and substitution derivatives thereof (e.g., poly(3,4-ethylenedioxythiophene)).

[0020]

When the semiconductor used has an electrical conductivity of  $10^{-1}$  to  $10^3$  S/cm, the produced capacitor can have a small ESR value and this is preferred.

In the solid electrolytic capacitor of the present invention, an electrically conducting layer may be formed on the semiconductor layer formed by the above-described method, so that good electrical contact with the external drawing-out lead (for example, lead frame) can be obtained.

[0021]

The electrically conducting layer can be formed, for example, by the solidification of an electrically conducting paste, plating, metallization, or formation of a heat-resistant electrically conducting resin film. Preferred examples of the electrically conducting paste include silver paste, copper paste, aluminum paste, carbon paste and nickel paste, and these may be used individually or in combination of two or more thereof. In the case of using two or more pastes, the pastes may be mixed or may be superposed one on another as separate layers. The electrically conducting paste applied is then solidified by

allowing it to stand in air or under heating. Examples of the plating include nickel plating, copper plating, silver plating and aluminum plating. Examples of the metal vapor-deposited include aluminum, nickel, copper and silver.

More specifically, for example, carbon paste and silver paste are stacked in this order on the another electrode and then, the entire is molded with a material such as epoxy resin, thereby fabricating a solid electrolytic capacitor.

[0022]

The capacitor having such a constitution of the present invention is jacketed, for example, by resin mold, resin case, metallic jacket case, resin dipping or laminate film and thereby, can be completed as a capacitor product for various uses.

The capacitor produced in the present invention can be preferably used, for example, for circuits using a high-capacitance capacitor, such as electric power circuit. These circuits can be used in various digital devices such as personal computer, sever, camera, game machine, DVD, AV equipment and cellular phone, and electrical devices such as various electric power sources. The solid electrolytic capacitor produced in the present invention is low in the leakage current after packaging and therefore, by using this solid electrolytic capacitor, electronic circuits and

electronic devices having less initial failure can be obtained.

[0023]

[Examples]

The present invention is described in greater detail below by referring to Examples, however, the scope of the present invention is not limited by these Examples.

[0024]

Examples 1 to 8:

A niobium primary powder (average particle size: 0.8  $\mu\text{m}$ ) ground by utilizing the hydrogen embrittlement of a niobium ingot was granulated to obtain a niobium powder having an average particle size of 100  $\mu\text{m}$  (this was a fine powder and therefore, naturally oxidized to contain 35,000 ppm of oxygen). The obtained niobium powder was left standing in a nitrogen atmosphere at 500°C and then in Ar at 700°C to provide a partially nitrided niobium powder (CV: 82,000/g) having a nitrided amount of 10,000 ppm. The resulting niobium powder was molded together with a 0.29 $\phi$  niobium wire and then sintered at 1,320°C. In this way, a plurality of sintered bodies (anodes) having a size of 4.0x3.5x1.7 mm (weight: 0.08 g) were produced. Each sintered body was electrochemically formed in an aqueous 0.1% phosphoric acid solution for 7 hours under conditions of 80°C and 18 V to form a dielectric layer mainly

comprising niobium oxide on the anode surface. The resulting anode having formed thereon a dielectric layer was heat-treated by leaving it in a furnace at a temperature shown in Table 1 under atmospheric pressure and thereafter, re-electrochemically formed in an aqueous 0.1% phosphoric acid solution under conditions of 80°C and 13 V. The re-electrochemical formation time, the number of operations of performing heat-treatment and re-electrochemical formation, and the LC value after final re-electrochemical formation are shown in Table 1. Subsequently, the anode was subjected to electrolytic polymerization in an aqueous solution having dissolved therein a pyrrole monomer and anthraquinonesulfonic acid to form a semiconductor (cathode) comprising polypyrrole. After sequentially stacking carbon paste and silver paste in the cathode side, the stacked body was placed on a separately prepared lead frame working out to an external electrode such that the lead wire in the anode side and the silver paste part in the cathode side were lying on two protruded portions of the lead frame, respectively. The lead wire in the anode side and the silver paste part in the cathode side were then electrically mechanically connected by spot-welding for the former and with silver paste for the latter. Thereafter, the entire excluding a part of the lead frame was transfer-molded with epoxy resin



and the lead frame outside the mold was cut and worked to produce a chip solid electrolytic capacitor having a size of 7.3×4.3×2.8 mm.

[0025]

Example 9:

Solid electrolytic capacitors were produced in the same manner as in Example 1 except that in Example 1, all heat-treatments were performed in water vapor.

[0026]

Example 10:

Solid electrolytic capacitors were produced in the same manner as in Example 1 except that in Example 1, all heat-treatments were performed in a furnace filled with a 15% oxygen gas diluted with argon gas.

[0027]

Example 11:

Solid electrolytic capacitors were produced in the same manner as in Example 1 except that in Example 1, the CV value of niobium powder used was changed to 120,000/g, all heat-treatments were performed in a furnace filled with a 45% oxygen gas diluted with argon, and the electrolytic polymerization was performed by using an ethylenedioxythiophene monomer in place of the pyrrole monomer to change the semiconductor to polyethylenedioxythiophene.

[0028]

Comparative Examples 1 to 4:

Solid electrolytic capacitors were produced in the same manner as in Example 1 except that neither heat-treatment nor re-electrochemical formation was performed (Comparative Example 1), re-electrochemical formation was performed once without performing heat-treatment (Comparative Example 2), heat-treatment was performed but re-electrochemical formation was not performed (Comparative Example 3), or heat-treatment and re-electrochemical formation each was performed once (Comparative Example 4).

[0029]

Comparative Example 5:

Solid electrolytic capacitors were produced in the same manner as in Example 1 except that in Example 1, the heat-treatment temperature was changed to 180°C.

[0030]

Comparative Example 6:

Solid electrolytic capacitors were produced in the same manner as in Example 1 except that in Example 1, the re-electrochemical formation time was shortened to give an LC value of 1.1 nA/CV after the final re-electrochemical formation.

[0031]

The initial performance and LC value (4 V) after

packaging of each solid electrolytic capacitor produced in Examples 1 to 11 and Comparative Examples 1 to 6 are shown in Table 2. The packaging was performed by a method of attaching the solid electrolytic capacitor to a circuit board by cream soldering and passing the circuit board through a reflow furnace having a temperature pattern with a maximum temperature of 260°C (230°C, 30 seconds). The LC value after packaging was a value within 30 minutes after passing through the reflow furnace. The ESR value at 100 kHz after packaging was 40 mΩ in all capacitors. In each Example, the value is an average of n=30 units.

[0032]

[Table 1]

TABLE 1

		Heat Treatment		Re-Electrochemical Formation Time, min.	Total Number of Operations (times)	LC/CV after Final Re-Electrochemical Formation, nA/ $\mu$ FV
		Temperature, °C	Time, min.			
Example	1	250	10	10	40	0.13
	2	250	100	10	40	0.18
	3	290	10	10	30	0.12
	4	290	100	10	30	0.17
	5	290	10	50	30	0.09
	6	380	10	10	15	0.20
	7	500	10	100	10	0.51
	8	210	10	10	55	0.23
	9	250	10	10	40	0.12
	10	250	10	10	40	0.10
	11	250	10	10	40	0.24
Comparative Example	1	-	-	-	0	1.12
	2	-	-	10	0	0.14
	3	250	10	-	0	1.61
	4	250	10	10	1	0.40
	5	180	10	10	40	0.16
	6	250	10	10	40	1.10

[0033]

[Table 2]

TABLE 2

		Initial Value of Product Capacitance, LC, $\mu\text{A}$ $\mu\text{F}$		LC After Packaging, $\mu\text{A}$
Example	1	328	17	43
	2	330	21	53
	3	325	15	41
	4	320	20	55
	5	326	13	40
	6	318	16	58
	7	307	15	71
	8	333	19	57
	9	320	17	34
	10	321	16	36
	11	466	26	66
Comparative Example	1	323	128	1231
	2	330	19	287
	3	322	215	1634
	4	334	15	186
	5	328	28	179
	6	319	184	480

[0034]

As seen from comparison of results between Examples 1 to 7 and Comparative Examples 1 to 4, when the operation of heat-treating and then re-electrochemically forming the anode having formed thereon a dielectric layer is performed twice or more, the LC value after the packaging is improved.

Also, as seen from comparison of results between Examples 1 to 7 and Comparative Example 5, when the heat-treatment temperature is 200°C or more, the LC value after packaging is improved, which is the object of the present invention. Furthermore, as seen from comparison of results between Examples 1 to 7 and Comparative Example 6, when the LC/CV value after re-electrochemical formation is set to 1 nA or less, the LC value at the initial stage of the manufactured solid electrolytic capacitor product is improved and the LC value after packaging is also improved.

[0035]

[Effects of the Invention]

According to the production method of the present invention, comprising repeating twice or more the steps of exposing the dielectric layer to a temperature of 200 to 1,000°C and then re-electrochemically forming the dielectric layer before the cathode comprising an organic semiconductor is formed, a solid electrolytic capacitor improved in the leakage current (LC) value after packaging can be obtained.